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The structure of lead silicate glasses determined by vibrational spectroscopy

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The polarized Raman spectra and infrared powder absorption spectra for $PbO \cdot xSiO_2$ glasses, with $0.5 \leqslant x \leqslant 2$, were measured and interpreted in terms of the structure of the glasses. Comparison of the spectra of the glasses with the spectra of numerous stable and metastable crystalline phases was also made. It was found that the glasses are composed of a number of silicate species. In glasses for which x is less than 1, the presence of ionic oxygen (oxygen not bonded to silicon) is confidently inferred from the spectra. A new way of deconvoluting the spectra is also reported.

1. Introduction

This paper reports a study of lead silicate glasses by Raman and infrared spectroscopy. Glass formation extends from SiO_2 to 67 mol% PbO and beyond. The glasses are liable to devitrify upon annealing between 400 and 700° C. Metastable phases result from devitrification of compositions between the orthosilicate and the metasilicate. Raman spectra of these are reported elsewhere [1]. Lead silicate glasses of high PbO concentration have very low softening points, large thermal expansion coefficients, and high refractive indices, and are useful as solder glasses, for glass-to-metal seals and, of course, as optical glass. On account of the scientific and technological interest in this system, it is natural to inquire about the structure of such glasses. Mydlar *et al* [2] have studied some of the lead silicate glasses and crystals by X-ray diffraction. They established that for compositions between the *ortho-* and *meta*-silicates, the range of nearest-neighbour Pb–Pb separations is independent of composition and narrowly distributed about a mean of 3.8 Å. The Pb–Pb distances in PbO (red) and lead metasilicate crystal are 3.8 Å and 3.5 to 3.8 Å respectively. The fact that the Pb–Pb nearest neighbour distances are highly correlated in the glasses indicates that some definite structures exist and that these structures may be similar to the structures of some crystals. Unfortunately the structures of many of the crystalline lead silicates are unknown and so it is not possible to be exhaustive when comparing the structures of crystals and glass.

Leventhal and Bray [3] in an NMR study of lead silicate glasses and crystals found that the immediate environments of the lead ions are nearly identical to those of lead ions in crystals. Once again the lack of crystal structure information prevents detailed conclusions from being drawn.

Some physical properties, such as electrical conductivity [4, 5] and thermodynamic properties [6] suggest that significant structural rearrangements as a function of composition occur at the metasilicate composition, but it has not been possible to be specific about the nature of these alterations. Chromatographic studies [7–9] show that the glass and crystal of the orthosilicate composition is composed of polymerized silicate units. The range of metastable immiscibility is not very well known. Glasses with less than 30% PbO are expected to be phase separated [10, 11] and it has been reported [11] that a glass of composition $24.6PbO \cdot 75.4SiO_2$ is phase separated. Raman spectra of some $PbO–SiO_2$ glasses have been measured by Hagiwara and Oyamada [12] and Verweij and Konijnendijk [13].

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2. Experimental

2.1. Preparation of glasses

Glasses were prepared from reagent grade Pb_3O_4 (Baker Chemical Company) and SiO_2 (about 200 mesh silica floated powder, Fisher Scientific Company). Twenty- to thirty-gram batches were well mixed and melted in Pt-crucibles in an electric furnace between 800 and 900° C for 3 to 5 h. The melts were stirred a few times during melting. Glass rods of approximately 1 mm diameter were drawn from the melts. They were used for the Raman spectroscopic measurements without any further heat treatment. A small amount of fine glass powder for the IR absorption measurements was prepared by crushing the glass rods with an impact mortar, and then grinding with pestle and mortar.

2.2. Raman spectroscopic measurements

Raman spectra were measured on a Spex model 1401 double-grating spectrometer at a scattering angle 90°. The excitaion source was the 488 nm (20 492 cm^{-1}) line of a Spectra-Physics model 164 Ar-ion laser. The laser power could be varied as needed from 50 mw to 1500 mw. The Raman scattering geometry is shown in Fig. 1. The laser beam is propagated along the y-axis of the laboratory frame while the Raman scattered radiation is collected along the z-axis. Both polarized (xx) and depolarized (xy) spectra were recorded from the glass rods at 50 cm^{-1} min^{-1} scanning speed. The glass rods were all strained along the rod direction (x-direction in the experimental set-up), but the effect of the strain on the depolarization ratio was not significant for our study. The polarized and depolarized spectra at frequencies above 550 cm^{-1} were recorded at a scanning speed of 25 cm^{-1} min^{-1}. Data points were measured every 6.25 cm^{-1} and the data were analysed numerically as described in the next section. The depolarized spectra were recorded at higher gain and wider slit width than the polarized spectra in order to obtain significant scattering intensity. Because the high-frequency peak is broad and relatively featureless, the loss of resolution due to the wider slit is not significant.

2.3. Infrared spectroscopic measurements

Infrared absorption spectra between 300 and 1500 cm^{-1} were recorded on a Perkin-Elmer 621 grating IR spectrophotometer. About 1.5 mg of glass powder was mixed with 200 mg KBr and vacuum cold-pressed into a transparent pellet.

3. Results

3.1. Spectra of lead silicate glasses

In Fig. 2 the polarized (xx) and depolarized (xy) Raman spectra of three lead silicate glasses are shown. It is useful to divide the spectra into three

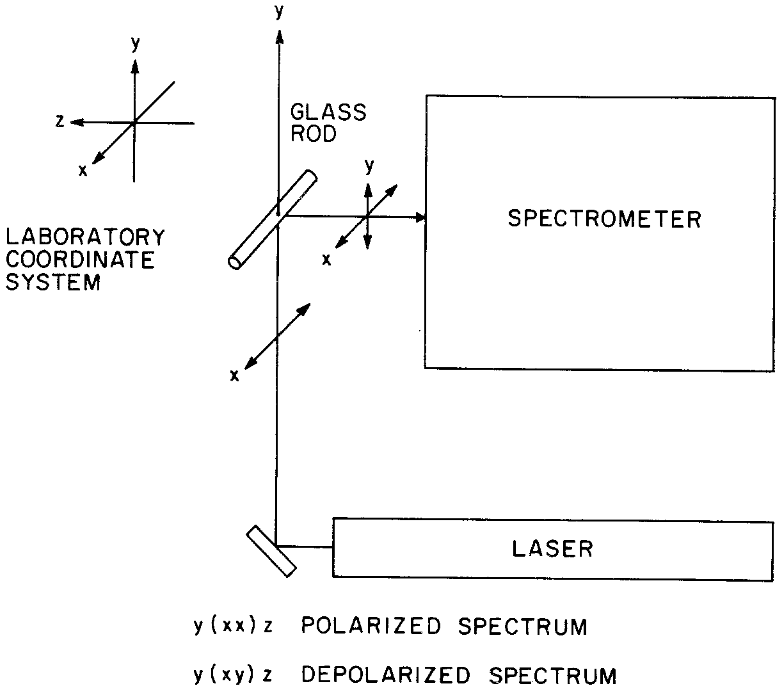


Figure 1 Sketch showing laboratory coordinates and sample geometry.

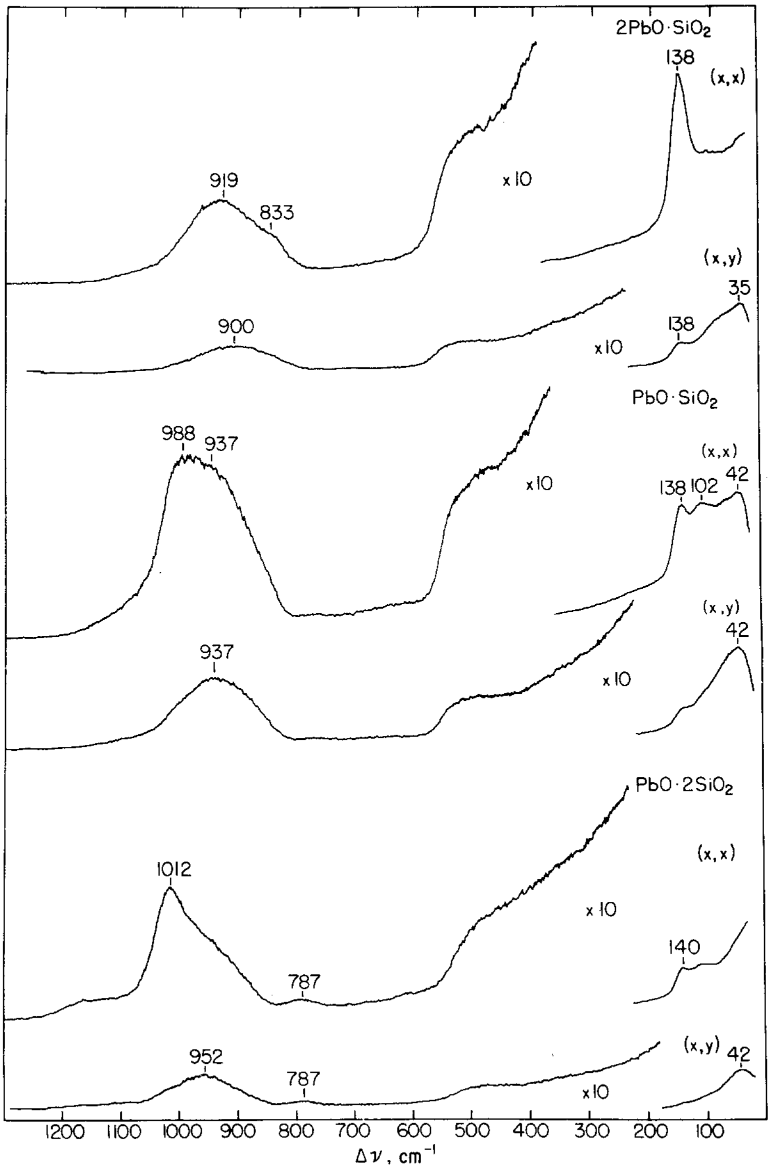


Figure 2 Polarized (*xx*) and depolarized (*xy*) Raman spectra of three lead silicate glasses.

regions and consider each region separately. The regions are; region I $\nu < 200\,\text{cm}^{-1}$; region II, $200 \leqslant \nu \leqslant 600\,\text{cm}^{-1}$; region III, $600\,\text{cm}^{-1} < \nu$.

The scattering from region I is about 5 to 10 times more intense than from regions II and III, as seen by the gain change in Fig. 2. The spectra in region I have bands at about 140, 100 and 40 cm^{-1} The broad band at 40 cm^{-1} is common to all glasses. It has been analysed in detail in vitreous silica by Stolen [14]. The Raman scattering is roughly proportional to the density of states, weighted by the appropriate temperature factor. (See also the discussion in [15].)

The other two bands in region I have approximate analogues in the spectra of several crystalline lead silicates, as will be seen later. For now we note that the intensity of the 140 cm^{-1} band increases with increasing PbO content (Fig. 3). The quantities I_{140} and I_{1000} are the maximum intensities of the (*xx*) Raman bands in the neighbourhood of 140 and 1000 cm^{-1} respectively. It is seen that as the PbO concentration is increased past the metasilicate, the intensity of the 140 cm^{-1} peak increases tremendously relative to the high-frequency intensity.

Region II consists of a broad featureless plateau terminating at about 500 cm^{-1}, which does not vary much with concentration. This scattering continuum is much more intense in parallel polarization.

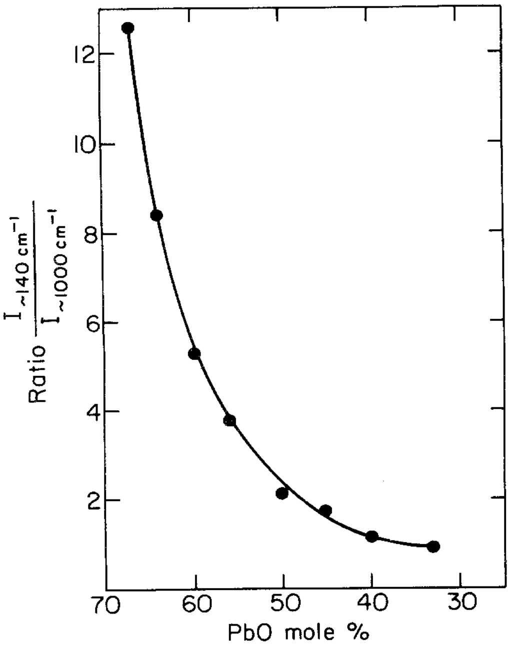


Figure 3 The ratio I_{140}/I_{1000} of the maximum intensity of the 140 cm^{-1} band to the maximum intensity of the band in the neighbourhood of 1000 cm^{-1}, for the (*xx*) spectra.

Region III consists of a broad asymmetric peak located between 850 and 1050 cm^{-1} depending on the composition. Detailed Raman spectra of region III are shown in Figs. 4a and 4b. Infrared spectra for regions II and III are shown in Fig. 5. The general features of the Raman spectra of region III are;

(a) The intensity of the polarized (*xx*) spectrum (for any composition) is about one order of magnitude greater than that of the depolarized (*xy*) spectrum, so the broad band of region III is largely polarized.

(b) The high-frequency bands of the (*xx*) and (*xy*) spectra as well as the infrared bands shift systematically to higher frequencies as the SiO_2 concentration is increased. For the smaller lead concentrations, increasing the PbO concentration brings about a rise in a shoulder at 910 cm^{-1} in the (*xx*) spectrum.

(c) The maximum of the (*xx*) peak is about 25 to 50 cm^{-1} higher than the maximum of the corresponding (*xy*) peak.

(d) As the PbO concentration increases beyond the metasilicate a band appears at about 840 cm^{-1} superimposed on the (*xx*) spectrum. This band is completely polarized and so does not appear in the (*xy*) spectrum.

The infrared spectra consist of two rather broad bands the frequencies of which depend on the glass composition. The high-frequency band, probably an envelope of Si–O asymmetric stretching modes, shifts from 900 cm^{-1} at the Pb_2SiO_4 composition to 1025 cm^{-1} at the disilicate composition. The band develops distinct shoulders and side bands at compositions between the metasilicate and disilicate. The second band occurs in the range of 490 to 470 cm^{-1}. Although the frequency shifts to lower values as the silica content of the glass increases, and band shape remains essentially the same over the entire composition range.

The Raman spectra of region III are very diffuse, and so several techniques were used to bring out some details of the spectra. First the small peak at 840 cm^{-1} was subtracted from the polarized spectra. The way in which this was done is illustrated in Fig. 4a. The dotted lines in that figure for any composition between the metasilicate and orthosilicate are estimates of the broad Raman bands in the region of 840 cm^{-1}. The 840 cm^{-1} band, presumably superimposed on the strong, broad band, was taken as the difference between the measured (*xx*) spectrum and the dotted line. The resulting difference bands are shown in Fig. 6a. They are somewhat assymmetric and are about 40 cm^{-1} wide at half maximum. The ratio I_{840}/I_{1000} of the intensity of the 840 cm^{-1} band to the maximum intensity of the (*xx*) band of region III is shown in Fig. 6b. As seen, the 840 cm^{-1} band appears abruptly at the metasilicate composition and its relative intensity increases uniformly with increasing PbO concentration.

Considering Fig. 4, it is seen that at the highest frequencies of region III, where $I_{(xy)}$ drops off sharply, the modes are completely polarized. The remainder of the spectra are slightly depolarized since $I_{(xy)} \ll I_{(xx)}$ but $I_{(xy)}$ is not zero. This suggests that the spectrum $I_{(xx)}$ is actually a superposition of the spectra of two groups of vibrational modes (excluding the modes giving rise to the 840 cm^{-1} band, which can be considered a third group). Of the two groups, the modes in one group are completely polarized while the modes in the other group are slightly depolarized. Each group consists of a large number of individual vibrational modes.

Given the information at hand, there is no unique way of separating the two groups of modes. The reason is that the ratio $I_{(xy)}/I_{(xx)}$, the de-

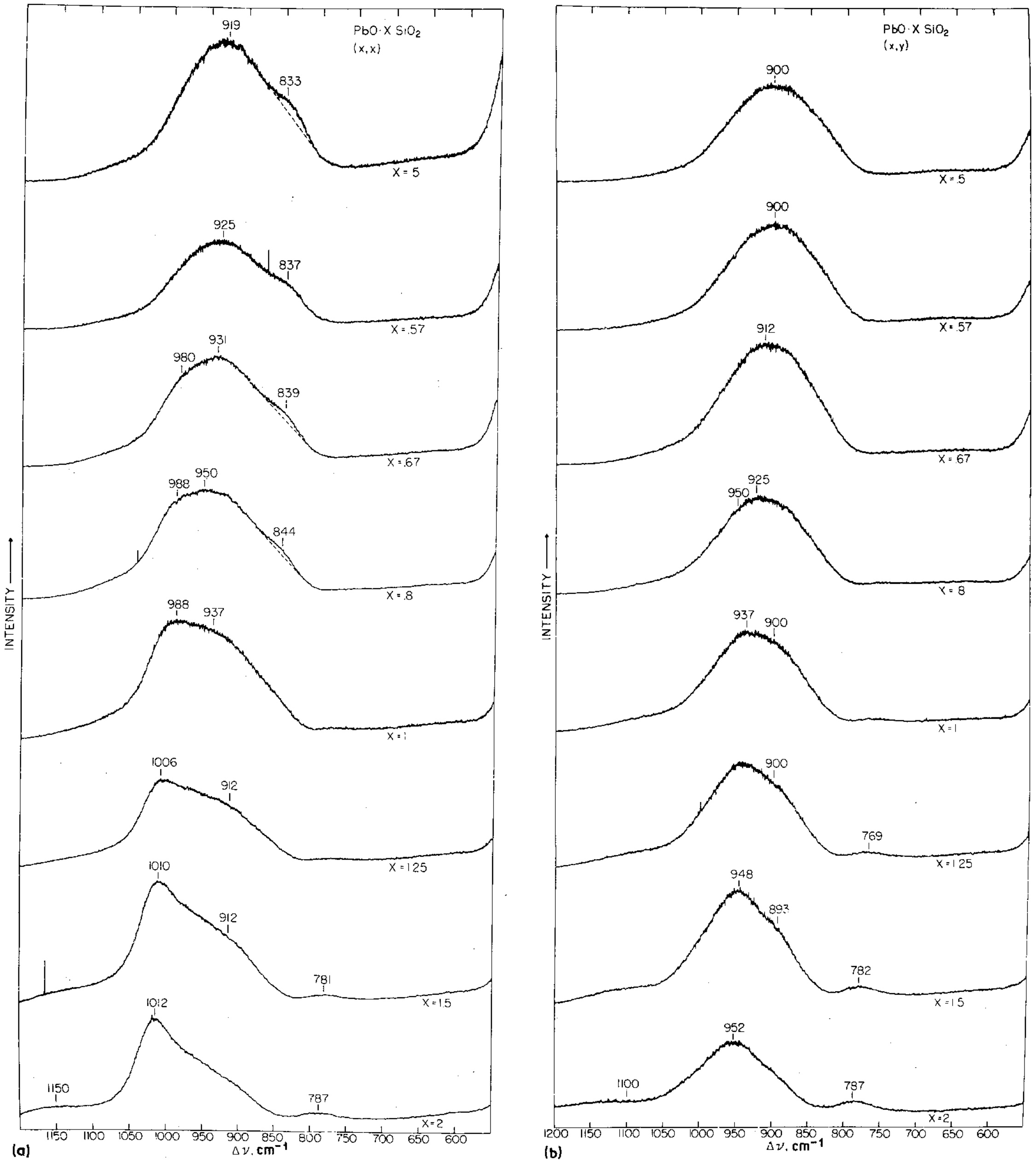


Figure 4 Details of the high-frequency Raman spectra of lead silicate glasses, (a) polarized spectra and (b) depolarized spectra. The dotted lines are explained in the text.

polarization ratio, depends on the particular normal mode of the glass. One way to separate the groups is to make the approximation that the amount of depolarization is a constant for all modes of the slightly depolarized group. Then we can deconvolute the spectra by subtracting from $I_{(xx)}$ that portion of $I_{(xx)}$ which has a depolarized part.

Our procedure is as follows: Let $I_{(xx)}$ be the polarized spectrum from which the 840 cm^{-1} band has already been subtracted out. Then let $I_{(xy)}$ be the observed (xy) spectrum. (All this is for region III only.) Let a and b be two constants and define

$$I'_{(xy)}(\omega) = a + bI_{(xy)}(\omega) \qquad (1)$$

The constants a and b are chosen so that over

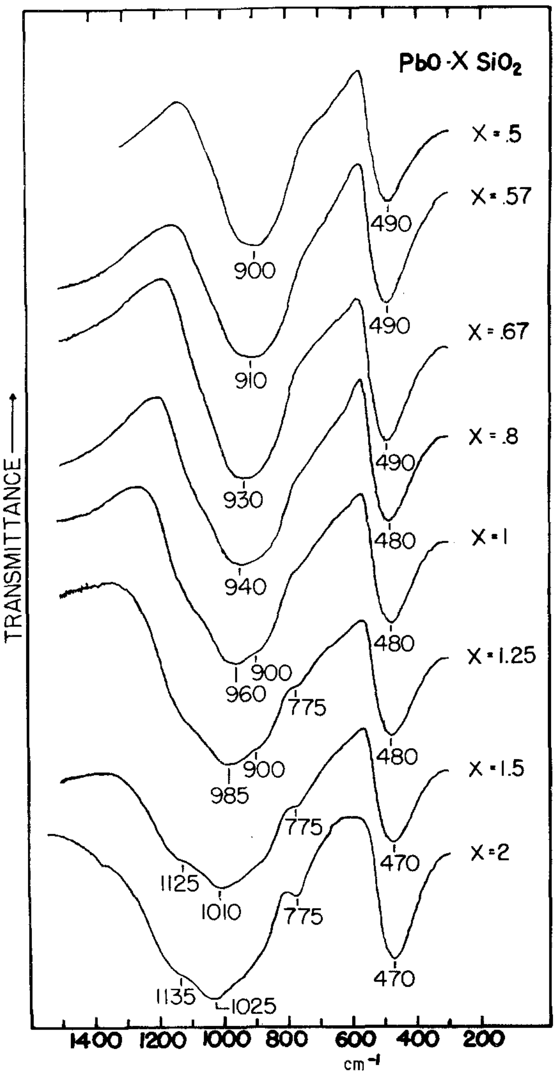


Figure 5 Infrared spectra of lead silicate glasses.

some selected frequency interval $[\omega_1, \omega_2]$ we have the equality

$$I'_{(xy)}(\omega) = I_{(xx)}(\omega) \qquad \omega_1 < \omega < \omega_2 \qquad (2)$$

Examination of Fig. 4 reveals that the low-frequency sides of the bands in both the polarized and depolarized spectra for a given composition are very similar. That is, the slopes $dI_{(xx)}/d\omega\,(\omega)$ and $dI_{(xy)}/d\omega(\omega)$ are approximately proportional to each other on the low-frequency side of the peaks. Thus $I_{(xy)}$ is scaled using Equation 1 so that it matches up with $I_{(xx)}$ over the frequency interval of this rapidly rising part. Then we form the difference spectrum over the entire frequency region III

$$I_{\text{pol}}(\omega) = I_{(xx)}(\omega) - I'_{(xy)}(\omega) \qquad (3)$$

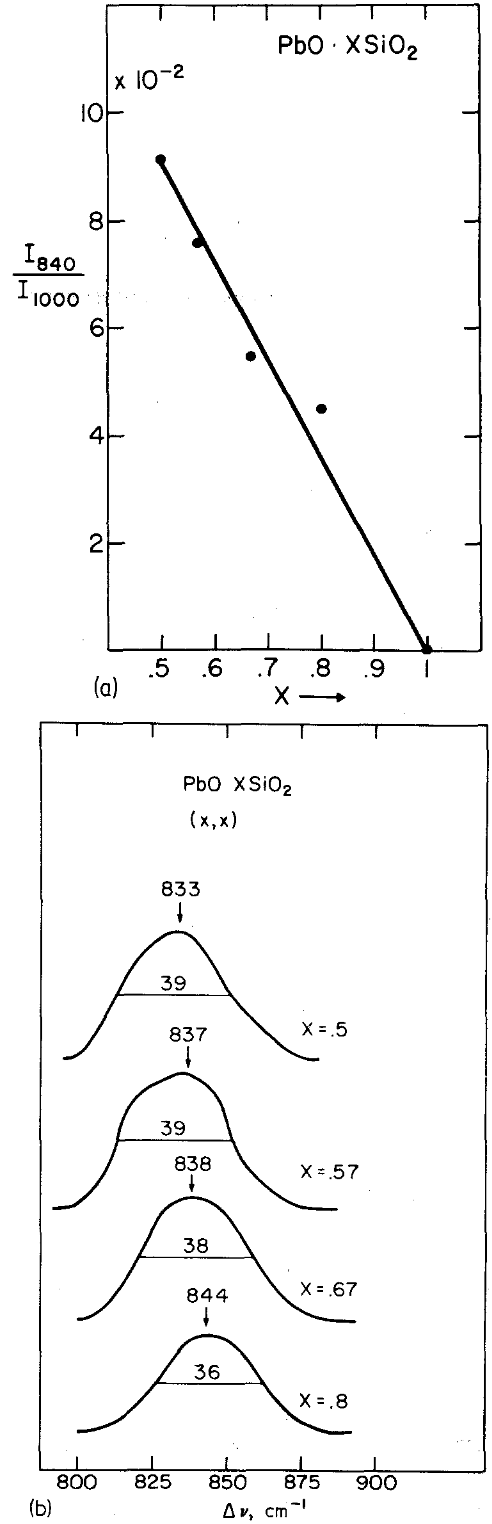
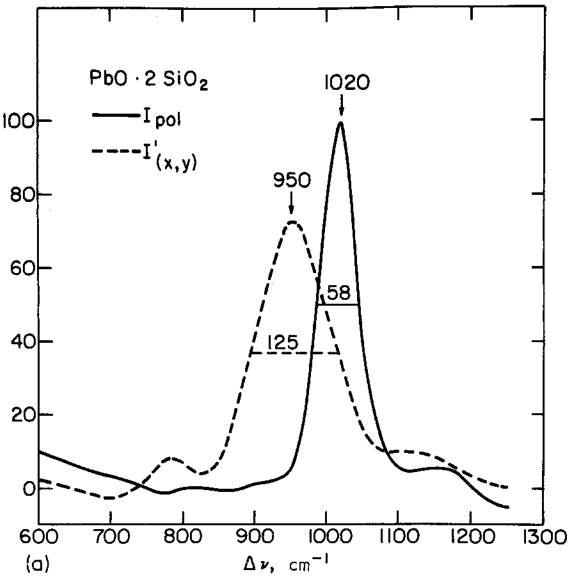
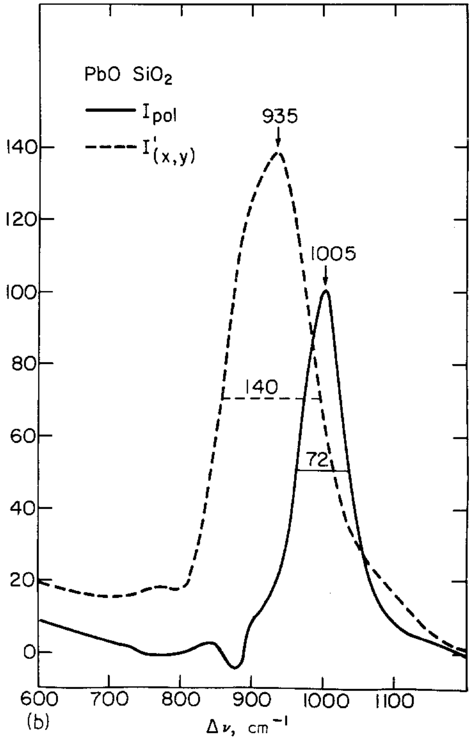


Figure 6 (a) Deconvoluted form of the 840 cm^{-1} band that occurs in the (xx) spectra. These spectra are the differences between the measured (xx) spectra and the dotted lines shown in Fig. 4a, (b) The ratio I_{840}/I_{1000} of the intensity of the 840 cm^{-1} band to that of the band in the neighbourhood of 1000 cm^{-1} for the (xx) spectra.





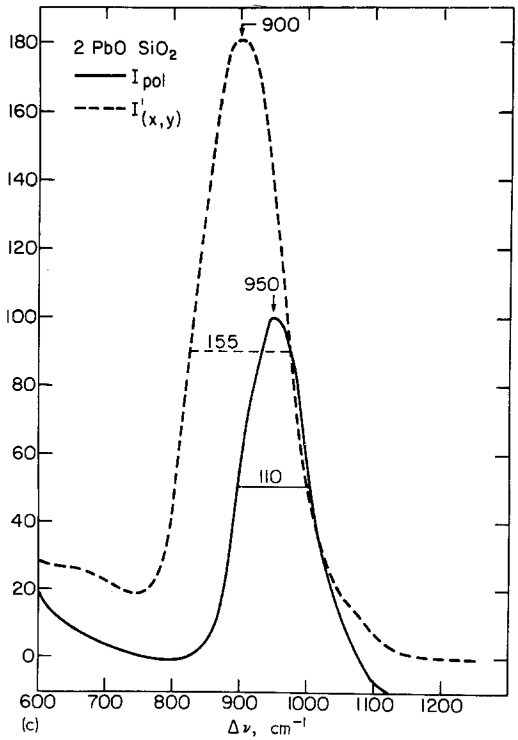


Figure 7 The functions I_{pol} and $I'_{(xy)}$ as explained in the text; (a) disilicate composition, (b) metasilicate compositon, (c) orthosilicate composition.

The resulting I_{pol} is presumably that fraction of the (*xx*) spectrum which is completely polarized (apart from the small 840 cm^{-1} peak).

Several of the resulting curves I_{pol} and $I'_{(xy)}$ are shown in Fig. 7. As can be seen, the completely polarized curve is nearly symmetrical, although the portion of the curve near the baseline is somewhat erratic. The curve I_{pol} obtained does depend to some extent on the precise frequency interval along which the relation (2) is taken to hold. The curves of Fig. 7 are minimized in the sense that the baseline is smoothest and closest to zero.

The curves shift systematically as a function of composition. The band frequencies of both I_{pol} and $I'_{(xy)}$ increase as the SiO$_2$ concentration increases, as shown in Fig. 8a. The rate of increase of band frequency decreases markedly at the metasilicate composition. This rapid variation is not seen in the infrared spectra, whose band positions are plotted in Fig. 8b. The discontinuities in the band frequency–composition plot reported by Hagiwara and Oyamada [12] were not observed. Furthermore, as seen in Fig. 8c the band width of I_{pol} decreases by nearly a factor of 2 between the orthosilicate and metasilicate while the width of $I'_{(xy)}$ decreases much less. The actual width of the depolarized band, however, is larger than the width of the polarized band. Finally in Fig. 8d the relative intensities at maximum of I_{pol} and $I'_{(xy)}$ are plotted as well as the approximate relative areas

$$I_{\mathrm{pol}} W_{\mathrm{pol}} / I'_{(xy)} W'_{(xy)}$$

where I is the intensity of the band at maximum

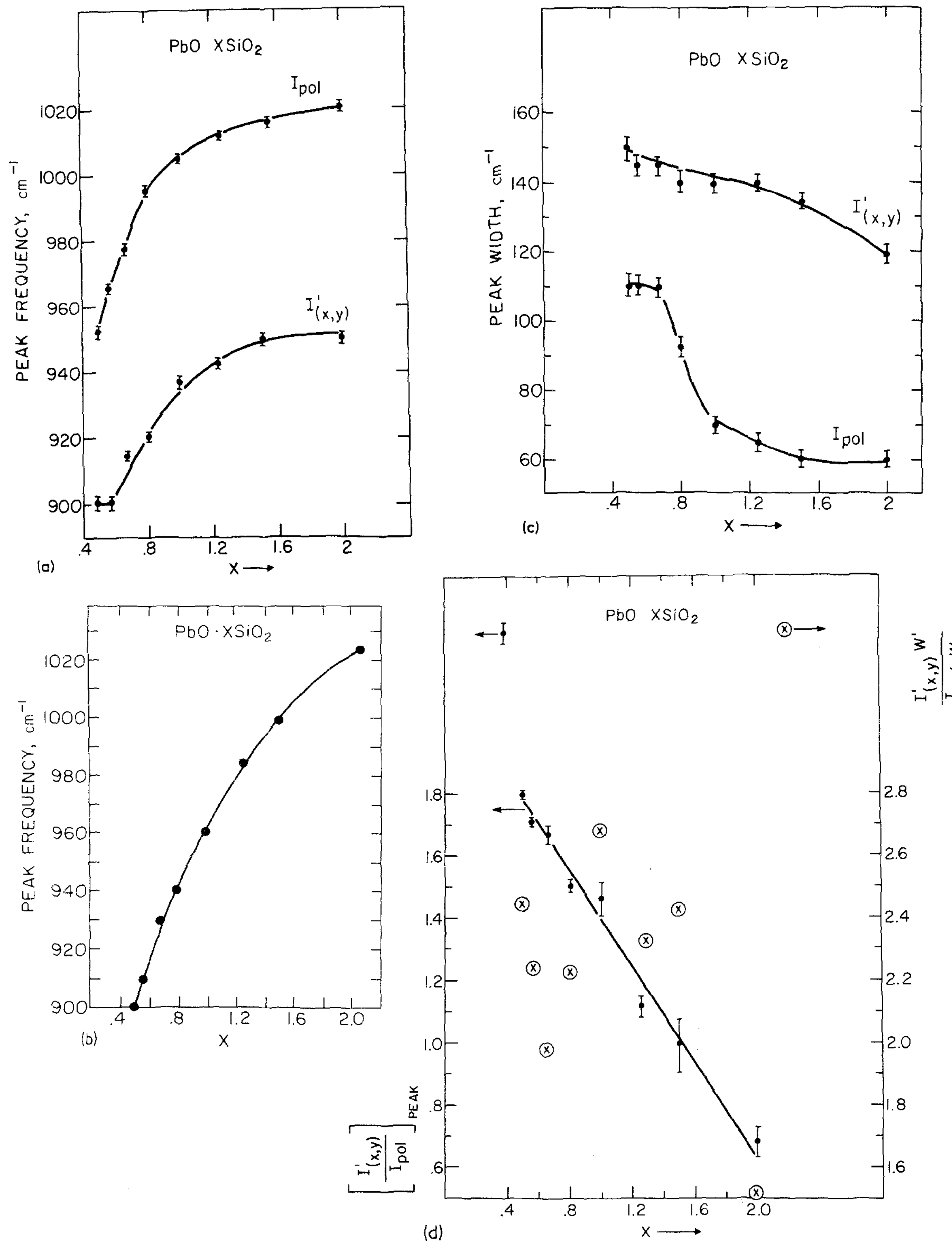


Figure 8 (a) Band frequencies of I_{pol} and $I'_{(xy)}$ as a function of composition, (b) Band frequencies of the infrared absorption as a function of composition, (c) Band widths of I_{pol} and $I'_{(xy)}$ as a function of composition. (d) Ratio of the maximum intensities of I_{pol} and $I'_{(xy)}$ (left scale) and the ratio of the approximate areas of these bands (right scale).

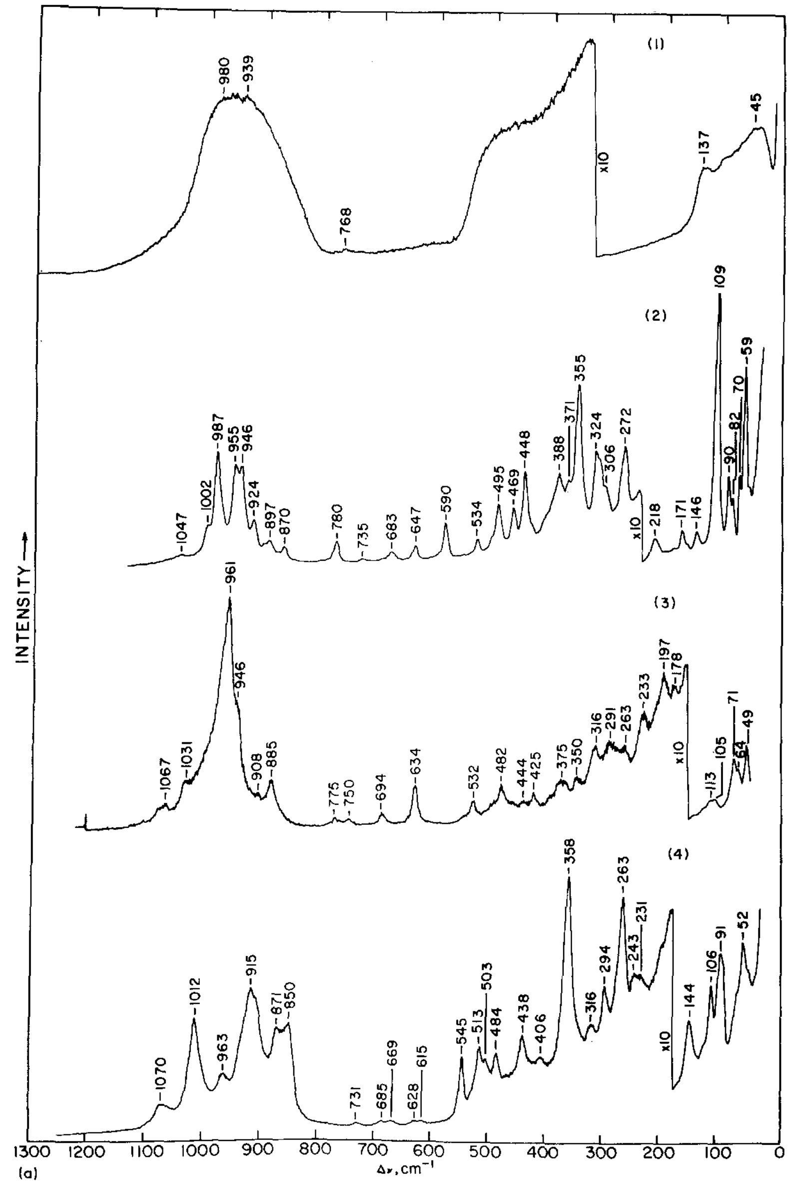


Figure 9 Raman (a) and infrared (b) spectra of lead metasilicate crystals and glass. Spectra are labelled; (1) glass, (2) alamosite, (3) L–$PbSiO_3$ and (4) hexagonal $PbSiO_3$.

and *W* is the half-maximum width of the band. It is seen that for this latter quantity there is considerable scatter, but to within a factor of 1.5 the ratio of the areas of the two bands are independent of composition.

3.2. Comparison of glass and crystal Raman spectra

In interpreting the vibrational spectra of lead silicate glasses, it is useful to make a comparison with the known Raman spectra of numerous crystalline and amorphous silicates in the alkali oxide–alkaline earth oxide–silica system. The high-frequency ($> 800\,\text{cm}^{-1}$) Raman spectra of crystalline silicates generally consist of one or two very strong, highly polarized bands, due to the symmetric stretches of the silicate groups of the solid. Sometimes, if the crystal symmetry is low, the strongly Raman active modes are split into groups. In this case we may refer to the central frequency of the group. The very strong symmetrical stretches are also observed in glass spectra, and so we pay

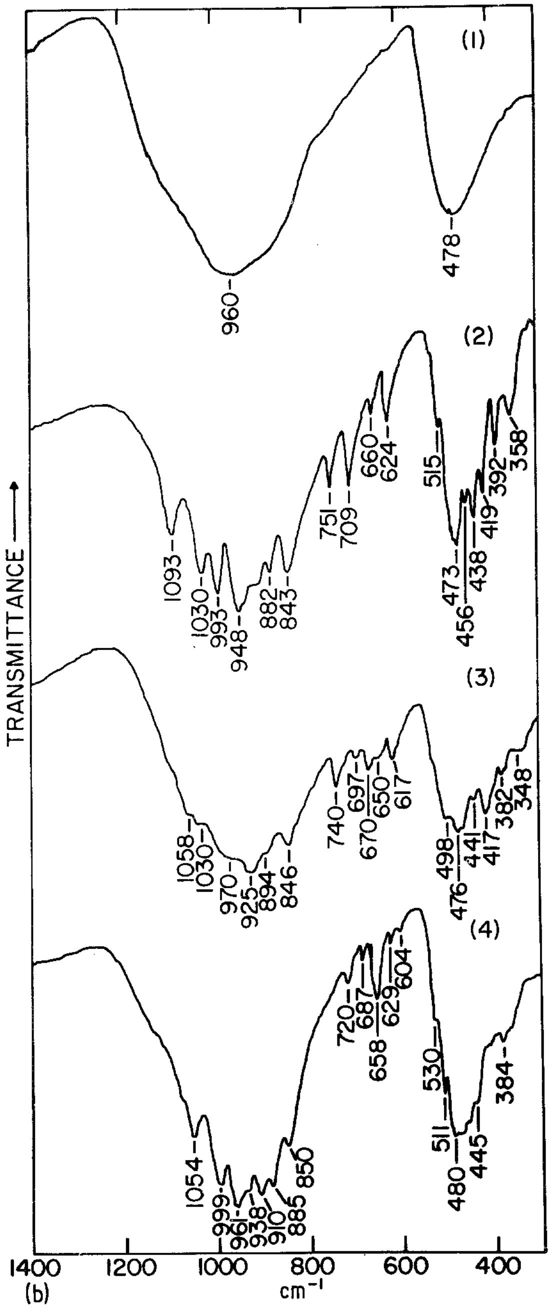


Figure 9 continued.

particular attention to such modes. The essential observation about these crystalline silicates is that the frequencies of the strong high-frequency Raman modes increase with increasing polymerization of the silicate network of the glass. There is a much weaker dependence on the other monovalent and divalent cations present.

In the case of alkali–alkaline earth–silicate glasses it has been shown [16] that the dominant high-frequency Raman bands of a crystal appear also in the Raman spectrum of the glass of similar composition. These bands are remarkably narrow and well defined. Theoretical calculations [17] based on a simplified model suggest that disordering the polymerized silicate units by randomly varying bond angles, but without breaking Si–O bonds, does not much alter the strong high-frequency Raman-active vibrations. As a result, comparison of the Raman spectra of glasses and crystals has been used extensively to deduce structural information about glasses. While there does not seem to be an impartial measure of the validity of this procedure, still it has been carried out self-consistently for a large number of glasses by various workers [13, 18–21].

Comparison of the Raman spectra of lead silicate crystals is made difficult by the fact that many modifications are known of lead orthosilicate, lead metasilicate and several intermediate compositions. There is substantial confusion concerning the number of polymorphs, their structural interrelationships, and their thermodynamic stability. These questions will be taken up elsewhere [1]. For the moment, the nomenclature on the crystalline phases in the sections that follow is that of Smart and Glasser [22].

Referring now to lead silicate glasses, the Raman spectra of lead metasilicate glass is compared with three of the known crystal forms in Fig. 9a. Alamosite is the only stable metasilicate crystal; the other two are metastable. Alamosite is known [23] to consist of parallel $(SiO_3)_n$ chains. There are 12 tetrahedra in the repeat unit and the chains are strongly buckled. Divalent lead in alamosite is in a pyramidal coordination, one triangular pyramid and two square pyramids. These are linked to form spiral chains parallel to [0 1 0]. The structures of the metastable metasilicates are not known. Since the dominant Raman band of L–$PbSiO_3$ is at 950 cm^{-1} the crystal probably consists also of $(SiO_3)_n$ chains. The spectra of hexagonal $PbSiO_3$ indicate a completely different crystal structure. Interestingly, the infrared spectra of all these crystals are similar to each other and to the IR spectrum of the glass.

As for the glass, the band of I_{pol}, the completely polarized Raman modes, is at 1005 cm^{-1}, indicating that probably some structures even more polymerized than chains are present. (Recall that the completely polarized symmetric stretch is the Raman mode most indicative of polymerization.)

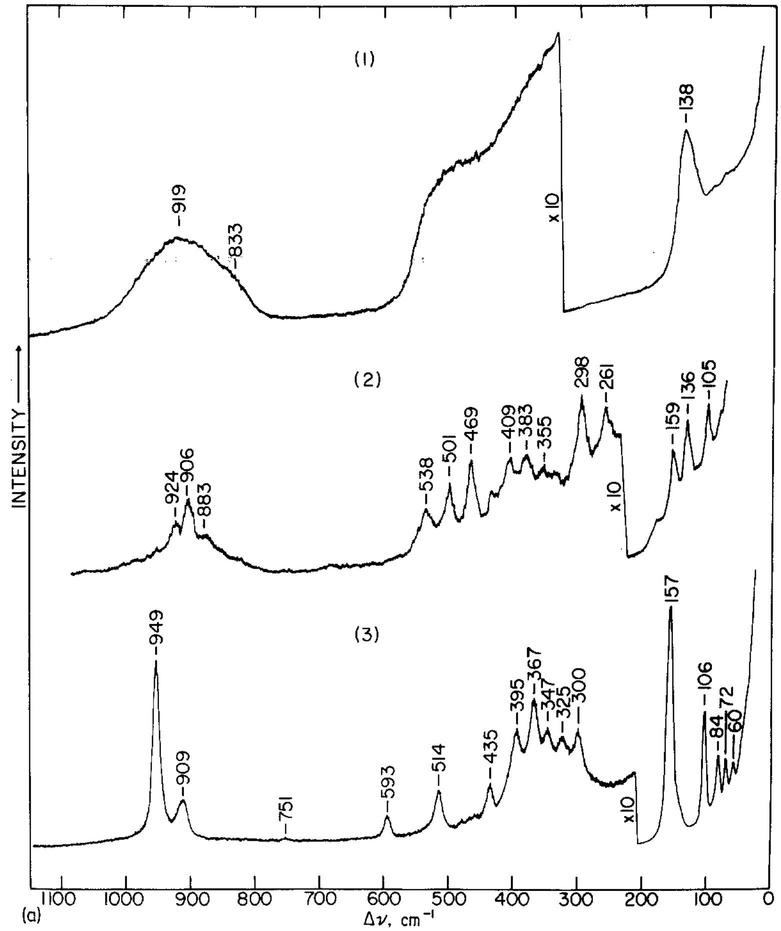


Figure 10 Raman (a) and infrared (b) spectra of lead orthosilicate crystal and glass. Spectra are labeled; (1) glass (2) L–Pb_2SiO_4, (3) H–Pb_2SiO_4. Nomenclature is that of Smart and Glasser [22].

Comparison of the crystal and glass Raman spectra of Fig. 9a and the infrared spectra of Fig. 9b indicates that the glass also consists of disordered $(SiO_3)_n$ chains. It appears that the glass spectrum is comparable to the spectra of both the stable metasilicate and to the metastable L–$PbSiO_3$.

The hexagonal metastable crystal appears to be unique. The hexagonal crystal is obtained by cooling the melt to around 650° C, while the L–$PbSiO_3$ is obtained by quenching to a glass and then reheating the glass. It is not clear why such different crystals are obtained in the two cases.

Consider now the orthosilicate composition $2PbO{\cdot}SiO_2$. The Raman spectra of the glass and two orthosilicate crystals are shown in Fig. 10a. The stable crystalline orthosilicates are H–Pb_2SiO_4 and M–Pb_2SiO_4. The L–crystal is metastable. However, the Raman and infrared spectra (Fig. 10) both indicate that the glass is closer in structure to the metastable L–Pb_2SiO_4 about whose structure nothing is known. The Raman and infrared spectra also indicate that the two crystalline orthosilicates differ significantly in structure.

Glasses between the compositions $5PbO{\cdot}3SiO_2$ and $3PbO{\cdot}2SiO_2$ when heated below about 600° C form a metastable crystalline phase or phases of unknown structure and disputed composition. The Raman spectra of the two end member compositions of "phase *X*" (Figs. 11a and b) are similar but not identical. The Raman spectra of the glasses of these compositions are identical to each other but distinctly different from the crystals. The infrared spectra of glasses and crystals are very similar. The Raman spectra of the crystalline phases are dominated by bands in the range of 850 to 870 cm^{-1} which are characteristic of SiO_4 groups. These bands are less prominent in the spectra of glasses.

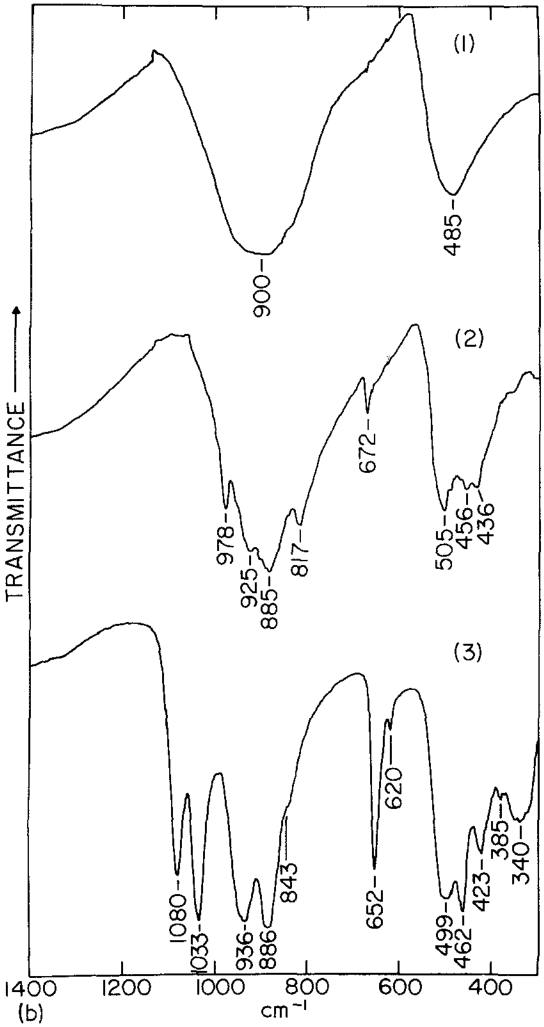


Figure 10 continued.

4. Discussion of glass structure

The overall impression of the glass structure as deduced from the Raman spectra (Figs. 2 and 4) is one of great structural disorder compared with other binary glasses such as the alkali silicates and alkali borates. The high-frequency bands are very broad and there is little variation in the form of the spectra as the composition is varied. In part the large Raman width is due to the depolarized component; the widths of the polarized components are comparable to those of the more disordered alkali silicate glasses [16]. Both IR and Raman band frequencies vary continuously across the composition range (Figs. 8a and b).

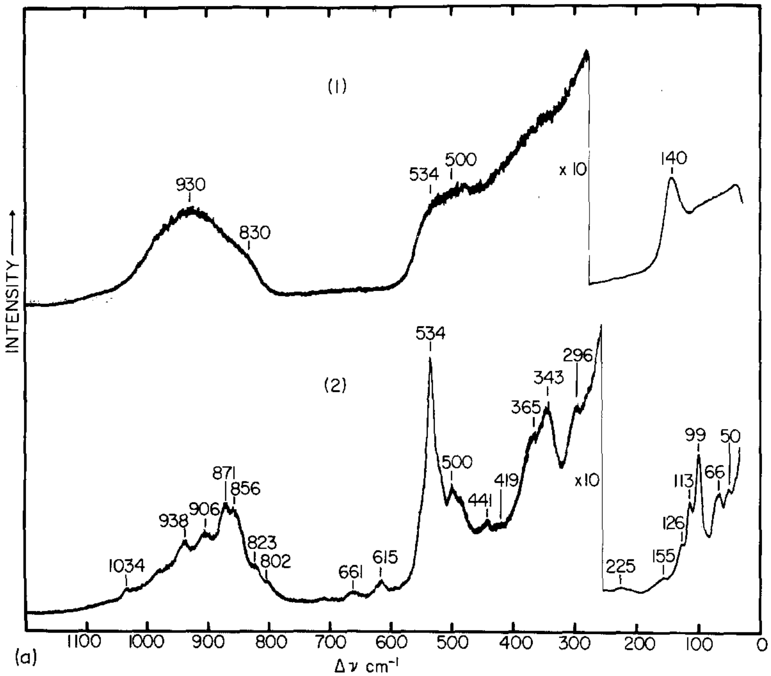
4.1. The orthosilicate composition

The structural unit in alkali and alkaline earth orthosilicates is the structurally isolated SiO_4 tetrahedron. All oxygens in these structures are non-bridging. Such compositions do not readily form glasses. The Raman spectra of many such structures exhibit strong bands in the region of 825 to 850 cm^{-1} [24] although there are exceptions such as zircon, where the main Raman band is as high as 1000 cm^{-1}. In general however, the centre of the strong Raman band of the lead orthosilicated glass at 900 to 920 cm^{-1} seems to be too high for isolated SiO_4 tetrahedra and some degree of polymerization of the tetrahedra is required. This would be consistent with the glass-forming behaviour of the $2PbO \cdot SiO_2$ composition. The infrared band at 900 cm^{-1} is in about the range found in crystalline orthosilicates [25].

It is possible that the completely polarized band at 840 cm^{-1} in the spectrum of lead orthosilicate glass is due to the presence of some isolated SiO_4 tetrahedra. Fig. 6b shows that SiO_4 anions begin to appear at the metasilicate composition and their number increases monotonically as the PbO concentration increases.

It is also clear from Fig. 4 that the 840 cm^{-1} band accounts for only a small portion of the total Raman spectrum. We take this to mean that SiO_4^{4-} anions form only a part of the glass structure. As for the remainder of the spectrum, we suggest that the dominant high-frequency Raman band is due largely to the vibrations of polymerized silicates. Considering the variation of Raman spectra with composition, it is seen that as the PbO concentration is increased beyond the metasilicate, the Raman band of the lead silicate glasses shifts continuously downward in frequency (cf Fig. 8a). This shift must be due to the depolymerization of the Si–O network from that characteristic of metasilicate chains to more disconnected silicates. The fact that the band exists in the Raman spectrum of the orthosilicate glass means that depolymerization is not complete. The completely polarized peak I_{pol} for lead orthosilicate glass is at 950 cm^{-1} (Fig. 7c) implying that Si_2O_7 units, and probably some larger groups, are present. It is not possible for isolated SiO_4 tetrahedra to give rise to a polarized band at 950 cm^{-1}.

If this interpretation is correct, simple valence considerations require the existence in the glass of ionic oxygen which is not bonded to silicon cations. It is interesting to speculate that these oxygens may be associated with lead ions to form the square pyramids found in alamosite, lead oxides, and other lead compounds, but no explicit



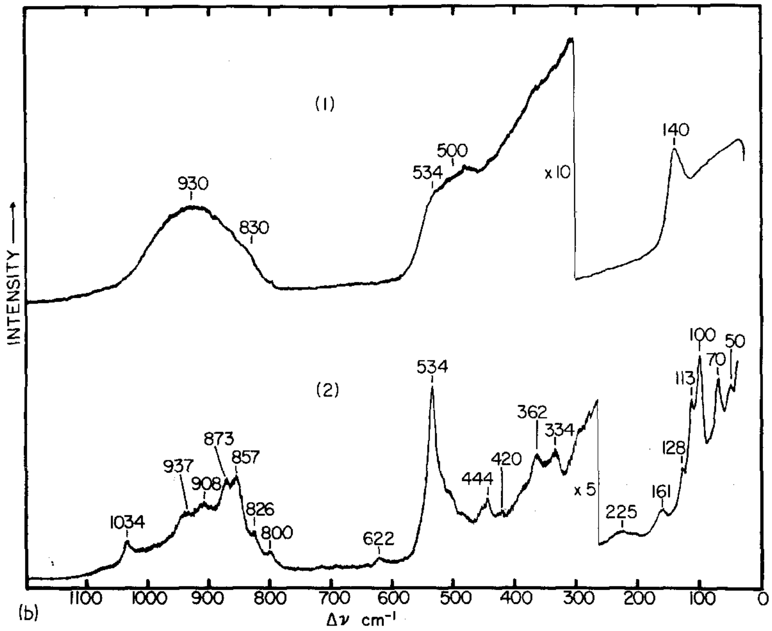


Figure 11 (a) Raman spectra of (1) glass and (2) crystal of the $5PbO{\cdot}3SiO_2$ composition, (b) Raman spectra of (1) glass and (2) crystal of the $3PbO{\cdot}2SiO_2$ composition, (c) IR spectra of (1) glass and (2) crystal of $3PbO{\cdot}2SiO_2$ composition. All crystal phases appear as "Phase *X*" in the literature.

evidence for this can be deduced from the Raman spectrum itself.

In short, then, the Raman spectra indicate the presence of three types of structures in lead orthosilicate glass; (a) isolated SiO_4 tetrahedra, (b) more polymerized silicate units and (c) ionic oxygen not bonded to silicon. The relative quantities of these species cannot be ascertained from the Raman spectra. In particular, the fact that the 840 cm^{-1} band is much weaker than the rest of the high-frequency Raman band does not necessarily mean that only a small number of isolated tetrahedra are present. The reason is that the Pb^{2+} ion is very polarizable and affects the Raman intensities of the various modes in an unknown manner.

It appears that lead orthosilicate glass is a mixture of a number of different types of structures. It follows that the same can be said for

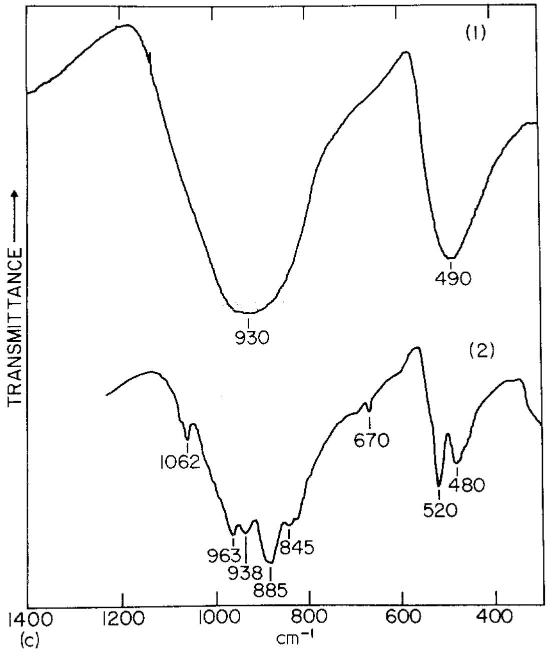


Figure 11 continued.

glasses of smaller PbO concentrations than the orthosilicate. The structure of lead orthosilicate glass in particular is considerably more complex than the chemical formula and comparison with alkali and alkaline earth orthosilicates would indicate. It is possible that the existence of a variety of structures is responsible for the glass forming ability of lead orthosilicate as well as for the large number of metastable phases. As far as we are aware, no single-component alkali or alkaline earth orthosilicate has been reported to form a glass by quenching from the melt.

4.2. The metasilicate composition

The high-frequency band in the IR spectrum shifts continuously through the metasilicate composition (Fig. 8b). Both polarized and depolarized components of the Raman band which have been changing frequency rapidly between the orthosilicate and metasilicate composition change much more slowly at silica concentrations higher than that of the metasilicate (Fig. 8a). The linewidth of the polarized component of the Raman band narrows rather abruptly at this composition (Fig. 8c). The above combined with the close resemblance between the Raman spectrum of the glass and that of crystalline alamosite and L–$PbSiO_3$ lend credence to the proposal that the metasilicate glass is primarily composed of chains although the large linewidths indicate that the chains are considerably disordered.

4.3. The disilicate composition

Finally consider glasses between the disilicate ($PbO \cdot 2SiO_2$) and the metasilicate. The high-frequency Raman band for these glasses, Fig. 4a, is considerably broader and occurs at a much lower frequency than in the case for alkali silicate glasses. In alkali-alkaline earth disilicate glass there are two high-frequency Raman bands, a very strong one at 1100 cm^{-1} and another weaker one at 950 cm^{-1}. As alkali concentration is increased, the frequency of the strong band shifts downward a small amount, and the intensity of the 950 cm^{-1} band increases tremendously relative to the intensity of the 1100 cm^{-1} band.

For the lead silicates, the rise of the shoulder at 912 cm^{-1} with increasing PbO concentration may be analogous to the increase of the 950 cm^{-1} band in the alkali silicates. In the case of lead disilicate, the very low band frequency (the band of I_{pol} is at 1020 cm^{-1}, Fig. 7c) suggests that lead disilicate is not composed primarily of $(Si_2O_5)_n$ sheets as is the case for the alkali–alkaline earth disilicates. It is probable that in the high-frequency region the Raman spectrum of lead disilicate is due primarily to silicates which are less polymerized than $(Si_2O_5)_n$ sheets. If this is indeed the case, then valence considerations require the existence of regions which are more polymerized than $(Si_2O_5)_n$ sheets. Such regions are known to be very weak Raman scatterers at high frequency [15] and their spectra would not be visible in comparison with that of less polymerized units. Thus the Raman spectrum is due primarily to the less polymerized regions. (A similar result was obtained for lithium silicates which were known to be macroscopically phase separated [16].)

It does not seem likely that the glasses between the disilicate and metasilicate are phase separated to any degree. The fact that the Raman spectra vary with composition means that the structure of the less polymerized regions of the glass also varies with composition. This would not be the case for phase separation.

4.4. Evidence for ionic oxygen

Finally, let us consider the behaviour of the band at 140 cm^{-1} (Fig. 3). The fact that this band emerges rapidly for increasing PbO concentration beyond the metasilicate indicates the formation of some structure in that composition region. It is tempting to associate this band with the vibrations of Pb–O units, the oxygen not being bonded to silicon (ionic oxygen). A similar band at 140 cm^{-1} was measured in yellow (orthorhombic) PbO and was reported also in red (tetragonal) PbO [26]. The existence of Pb–O units has already been inferred.

5. Summary

Our concept of the structure of lead silicate glasses is as follows; these glasses consist of a number of different silicate structures. There is no evidence that the glasses are actually phase separated on a large scale (say greater than 50 Å), although the possibility cannot be ruled out entirely. For compositions between the disilicate and the metasilicate, the glass is composed of regions polymerized both more and less than $(Si_2O_5)_n$ sheets. There do not seem to be many structures consisting of disordered $(Si_2O_5)_n$ regions. For compositions between the metasilicate and orthosilicate, the glass consists of some isolated SiO_4 tetrahedra, more polymerized silicate units and ionic oxygen (oxygen not bonded to a silicon). These glasses, then, are structurally very different from alkali–alkaline earth silicate glasses.

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